

We claim

1. A low dielectric constant polymer, comprising monomeric units derived from a compound having the general formula I

5



wherein

each X^1 is independently selected from hydrogen and inorganic leaving groups,
10 R^2 is an optional group and comprises an alkylene having 1 to 6 carbon atoms or
an arylene,

R^1 is a polycycloalkyl group and

n is an integer 1 to 3

15 2. The polymer according to claim 1, wherein the organic content of the polymer is in the range of 30 to 70 wt.-%, preferably higher than 48 wt.-%.

3. The polymer according to claim 1, wherein R^1 is a polycyclic alkyl group having from 9 to 16 carbon atoms.

20

4. The polymer according to claim 3, wherein R^1 is a cage compound.

5. The polymer according to claim 4, wherein R^1 is adamantyl or diadamantyl.

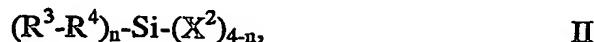
25 6. The polymer according to claim 5, wherein the adamantyl or diadamantyl is substituted with 1 to 3 alkyl substituents, which optionally carry 1 to 6 halogen substituents.

7. The polymer according to any of claims 1 to 6, wherein the inorganic leaving group is selected from halogens.

30

8. The polymer according to any of claims 1 to 7, obtainable by homopolymerization of compounds of the formula I.

9. The polymer according to any of claims 1 to 8, which is obtainable by copolymerization of a compound of formula I with a compound of formula II



5

wherein

X² is hydrogen or a hydrolysable group selected from halogen, acyloxy, alkoxy and OH groups,

R⁴ is an optional group and comprises an alkylene having 1 to 6 carbon atoms or
10 an arylene and

R³ is an alkyl having 1 to 16 carbon atoms, a vinyl having from 2 to 16 carbon atoms, a cycloalkyl having from 3 to 16 carbon atoms, an aryl having from 5 to 18 carbon atoms or a polycyclic alkyl group having from 7 to 16 carbon atoms,
and

15 n is an integer 1-3.

10. The polymer according to claim 9, wherein R³ is selected from alkyl groups having 1 to 6 carbon atoms, vinyl groups having from 2 to 6 carbon atoms, and aryl groups having 6 carbon atoms.

20

11. The polymer according to claim 9 or 10, wherein the molar ratio between monomeric units derived from compounds according to formula I and of formula II is in the range of 25:75 to 75:25.

25 12. The polymer according to any of claims 1 to 11, wherein R¹ or R³, respectively, is directly bonded to the silicon atom.

30 13. The polymer according to any of claims 1 to 11, wherein R¹ or R³, respectively, is bonded to the silicon atom via an alkylene chain selected from methylene, ethylene and propylene, or an arylene group selected from phenylene.

14. The polymer according to claim 1, wherein the total sum dielectric components at 1 MHz is 2.50 or less, preferably 2.1 or less.

15. The polymer according to claim 14, wherein the orientational dielectric constant of the polymer is 0.4 or less.

5 16. The polymer according to any of the preceding claims, wherein the oxygen content of the polymer is less than 15 atomic %.

17. The polymer according to any of claims 9 to 16, wherein the carbon content of the polymer is more than 25 atomic %.

10 18. The polymer according to any of the preceding claims, wherein the dielectric constant of the dielectric material after curing is 2.50 or less, preferably 2.30 or less.

15 19. The polymer according to any of the preceding claims, wherein the porosity of the dielectric material is less than 20 %, preferably less than 15 %.

20 20. The polymer according to claim 1, wherein the average pore radius is less than 1 nm.

21. The polymer according to claim 1, wherein the Young's modulus of the film is higher than 4 GPa after curing, in particular higher than 6 GPa.

20 22. A low dielectric constant polymer, comprising monomeric units derived from a compound selected from the group consisting of adamantyl trichlorosilane, adamantylpropyl trichlorosilane, 3,5,7-trifluoroadamantyl trichlorosilane, 3,5,7-trifluoromethyladamantyl trichlorosilane and adamantylphenyl trichlorosilane.

25 23. A method of forming a thin film having a dielectric constant of 2.5 or less, comprising

- hydrolyzing a first silicon compound having the formula I optionally with at least one second silicon compound having the formula II to produce a siloxane material;
- depositing the siloxane material in the form of a thin layer on a substrate; and
- curing the thin layer to form a film.

30 24. The method according to claim 23, wherein the substrate is a semiconductor substrate.

25. The method according to claim 23, wherein the dielectric material is provided on said semiconductor substrate in alternating areas with an electrically conductive material.

5 26. The method according to claim 25, wherein the electrically conductive material comprises aluminum or copper.

10 27. The method according to claim 25, wherein the alternating areas are formed by depositing and patterning the dielectric material, followed by depositing the electrically conductive material.

28. The method according to 27, wherein the depositing of the dielectric material and electrically conductive material is part of a copper damascene process.

15 29. The method according to claim 25, wherein the alternating areas are formed by depositing and patterning the electrically conductive material, followed by depositing the dielectric material.

20 30. The method according to any of claims 23 to 29, wherein the dielectric material is deposited on the substrate by a spin-on process, by spray-on, by dip coating or by chemical vapor deposition.

31. The method according to any of claims 23 to 30, wherein the dielectric material is subjected to annealing before curing.

25 32. The method according to any of claims 23 to 31, wherein the dielectric constant is further reduced by second thermal treatment step after the curing

30 33. The method according to claim 32, wherein the second thermal treatment is done with UV radiation.

34. The method according to any of claims 31 to 33, wherein the annealing is carried out by a process in which the material is subjected to electromagnetic radiation.

35. The method according to claim 34, wherein the electromagnetic radiation is selected from UV radiation, DUV radiation, Extreme UV radiation and IR radiation or a combination thereof.

5 36. The method according to claim 31, wherein the annealing is carried out by a process in which the material is exposed to an electron-beam

37. The method according to any of claims 31 to 36, wherein the dielectric material after annealing is subjected to said curing in an atmosphere of air, nitrogen, argon, forming gas or

10 vacuum.

38. The method according to any of claims 31 to 37, wherein after the annealing and curing steps the dielectric material comprises less than 0.001 wt% of silanols.

15 39. The method according to any of claims 31 to 38, wherein after the annealing and curing steps, the dielectric material is free of silanols.

40. The method according to any of claims 23 to 39, wherein after annealing of the dielectric material, a subsequent layer is deposited thereon, selected from a metal, a

20 diffusion barrier, a liner, a hard mask, or an additional dielectric layer.

41. The method according to any of claims 23 to 40, further comprising forming said dielectric material by preparing a siloxane composition by hydrolysis and condensation of selected precursors, applying the siloxane material on a substrate in the form of a layer,

25 patterning the layer by selective exposure to electromagnetic radiation or electron beam, developing the exposed layer, followed by said curing step.

42. The method according to any of claims 23 to 41, wherein the dielectric material has a dielectric constant of from 2.1 to 2.3.

30 43. The method according to any of claims 23 to 42, wherein the density of the dielectric material after curing is 1.2 g/cm³ or more.

44. The method according to any of claims 23 to 43, wherein the coefficient of thermal expansion of the dielectric material is less than 25 ppm/K, preferably less than 20 ppm/K, in particular less than 15 ppm/K.

5 45. The method according to any of claims 23 to 44, wherein the thermal decomposition temperature of the dielectric material is higher than 400 °C, in particular higher than 450 °C.

10 46. Composite material useful as low-k materials in dielectric applications, said materials comprising copolymers formed by copolymerisation of at least one comonomer having the formula



II

15 wherein

X₂ is hydrogen or a hydrolysable group selected from halogen, acyloxy, alkoxy and OH groups,

R₄ is an optional group and comprises an alkylene having 1 to 6 carbon atoms or an arylene and

20 R₃ is an alkyl having 1 to 16 carbon atoms, a vinyl having from 2 to 16 carbon atoms, a cycloalkyl having from 3 to 16 carbon atoms, an aryl having from 5 to 18 carbon atoms or a polycyclic alkyl group having from 7 to 16 carbon atoms, and

n is an integer 1-3,

25

with a silicon compound selected from the group of

a) silicon compounds having the general formula III

30



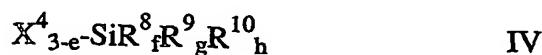
III

wherein X³ represents a hydrolyzable group; R⁴ is an alkenyl or alkynyl group, which optionally bears one or more substituents; R⁵ and R⁶ are independently selected from

hydrogen, substituted or non-substituted alkyl groups, substituted or non-substituted alkenyl and alkynyl groups, and substituted or non-substituted aryl groups; a is an integer 0, 1 or 2; b is an integer a+1; c is an integer 0, 1 or 2; d is an integer 0 or 1; and b + c + d = 3; is hydrolyzed;

5

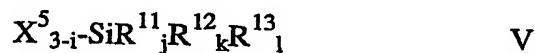
b) silicon compound having the general formula IV



10 wherein X^4 represents a hydrolyzable group; R^8 is an aryl group, which optionally bears one or more substituents; R^9 and R^{10} are independently selected from hydrogen, substituted or non-substituted alkyl groups, substituted or non-substituted alkenyl and alkynyl groups, and substituted or non-substituted aryl groups; e is an integer 0, 1 or 2; f is an integer e+1; g is an integer 0, 1 or 2; h is an integer 0 or 1; and f + g + h = 3; and

15

c) silicon compounds having the general formula V



20 wherein X^5 represents a hydrolyzable group; R^{11} is a hydrogen or an alkyl group, which optionally bears one or more substituents; R^{12} and R^{13} are independently selected from hydrogen, substituted or non-substituted alkyl groups, substituted or non-substituted alkenyl or alkynyl groups, and substituted or non-substituted aryl groups; i is an integer 0, 1 or 2; j is an integer i+1; k is an integer 0, 1 or 2; l is an integer 0 or 1; and j + k + l = 3,

25

with the proviso that copolymerisation is carried out using at least one comonomer having the formula II, wherein R_3 is polycyclic alkyl group having from 7 to 16 carbon atoms.

47. An electronic device containing a densified, dielectric material produced from a
30 material according to any of claims 1 to 22 or 46.

48. A method for forming a dielectric material having a dielectric constant of 2.6 or less, on a semiconductor substrate, comprising the steps of:

- introducing a monomeric, oligomeric or fully or partially polymerized deposition material on a semiconductor substrate by a spin-on or CVD method, said deposition material formed from a precursor material comprising a silicon-containing chemical compound having the formula I;
- 5 - forming a siloxane polymer film from the deposition material on the semiconductor substrate by activating polymerization and densification reactions by a curing process; and
- thereby forming a material on the semiconductor substrate having a relative dielectric constant lower than 2.6.

10

49. The method according to claim 48 comprising:

- providing on a substrate a dielectric material having a first density; and
- curing the dielectric material whereby the dielectric material is heated from a first temperature to a second temperature, to produce a dielectric material having a second density, which is lower than the first density by 10 % or more.

15

50. The method according to claim 48 or 49, comprising:

- providing on a substrate a dielectric material having a first elastic modulus; and
- curing the dielectric material whereby the dielectric material is heated from a first temperature to a second, to produce a dielectric material having a second elastic modulus, which is greater than the first elastic modulus by an amount of 50 % or more.

20

51. The method according to any of claims 48 to 50, comprising:

- providing on a substrate a dielectric material comprising a siloxane material; and
- curing the dielectric material whereby the dielectric material is heated from a first temperature to a second temperature, to produce a dielectric material having a coefficient of thermal expansion is less than 25 ppm/K.

25

52. The polymer according to any of claims 1 to 22 or prepared according to a method according to any of claims 23 to 51, wherein the pore diameter of the dielectric material is less than 2 nm, preferably less than 1.5 nm.

53. The polymer according to any of claims 1 to 22 or prepared according to a method according to any of claims 23 to 51, wherein the thermal stability of the dielectric material is better than 425 degC, preferably better than 450 degC.